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THE HYDROMETALLURGY OF COPPER, AND ITS SEPARATION FROM THE PRECIOUS METALS.

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WET processes for the extraction of copper from its ores have of late attracted much attention, especially in Europe, where the use of cupriferous iron-pyrites as a source of sulphur prevails. These processes present an additional interest, when, as is often the case, the copper-ores to be treated contain one or both of the precious metals, since the complete separation of these from copper, either in the dry or the moist way, is, as is well known, one of the difficult problems of metallurgy. The principal wet processes hitherto in use for the extraction of copper from its ores may be included under three classes:

I. Those in which the copper in sulphuretted ores is rendered soluble in water by calcining them, after a preliminary roasting which removes the greater part of their sulphur, with a portion of common salt, by which the copper is converted into a chloride (Longmaid and Henderson), or with sulphate of soda, by which sulphate of copper is formed (Monnier). Allied to these is the method by which a portion of the copper is got as soluble sulphate by roasting without addition, a process which is sometimes modified and rendered more complete by re-roasting the lixiviated residues with the addition of a portion of raw sulphuretted ore (Bankart).

II. Those methods in which free chlorhydric or sulphuric acid is used to dissolve the copper from oxydized or roasted ores. These, while simple and efficient, are too costly, except in certain localities where chlorhydric acid is a waste product. Related to them is the plan which consists in exposing the oxydized and moistened ores to the slow action of sulphurous acid mixed with air, by which a soluble sulphate of copper is formed. It has been proposed to decompose the solutions of sulphate or chloride of copper by sulphuretted bydrogen, thus separating the copper as sulphide, and using the liberated acid to dissolve fresh portions of oxydized copper. It

is, however, the almost universal practice to throw down the copper from its solutions, however obtained, in the metallic state by the use of iron, either scrap-iron or iron-sponge, although in some instances milk of lime has been used as a precipitant, by which oxide of copper is produced.

III. The method in which a hot solution of ferrous chloride, with common salt, is used to chloridize the oxydized copper and convert it into a mixture of cupric and cuprous chlorids, which latter, though nearly insoluble in water, is dissolved by help of the chloride of sodium. From this solution the copper is precipitated by metallic iron, thereby reproducing the ferrous chloride, and regenerating the solvent, an advantage which this process possesses over any other which gives the copper in the metallic form. This, which is known as the Hunt and Douglas method, may, in many cases, be used with advantage for the treatment of low-grade copper ores, and, as the neutral solvent does not dissolve either arsenic or antimony, enables fine copper to be got directly from ores holding these impurities.*

When, however, it is applied to the treatment of copper-ores containing silver, the use of the bath of ferrous chloride and chloride of sodium has, in common with the method of roasting with salt, the disadvantage that it converts the silver into a chloride which is soluble in a strong solution of chloride of sodium and is then with difficulty separated from the chlorides of copper. The separation of silver and copper when dissolved together in the state of chlorides has greatly exercised the ingenuity of metallurgical chemists from its importance in connection with the treatment of Spanish and Portuguese pyrites, now so extensively used in Great Britain as a source of sulphur, where their consumption in 1877 amounted to 600,000 tons. These ores contain on an average about forty-nine per cent. of sulphur and two or three per cent. of copper, with a little silver, equal, according to Claudet, to from twenty to twenty-eight grams to the ton of ore, and traces of gold. The residues after calcination still retain three or four per cent. of sulphur and about four per cent. of copper, with sixty per cent. or more of iron,

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* The hydrous silicate of copper (chrysocolla) is, like the carbonates of copper, completely decomposed by a hot solution of ferrous chloride with common salt. An account of the application of this method to the treatment of a crystalline hydrous silicate of alumina, magnesia, and copper (which is essentially a copper-chlorite, and has been described by the writer as a new species under the name of venerite), will be found in the Transactions of the American Institute of Mining Engineers, vol. iv, p. 328.

chiefly as peroxide. This material, after having been again calcined for some hours at a low heat in a reverberatory with about fifteen per cent. of common salt (or, as at Oker in Germany, with crude chloride of potassium), gives up to water acidulated with a little chlorhydric acid its sulphur as sulphate of soda, and its copper and silver as chlorides, together with a considerable excess of common salt, leaving behind a nearly pure peroxide of iron with not over two thousandths of copper. A minute portion of gold, which was converted into aurous chloride during the roasting, is also present in the solution.* The lixivium, in an example given by Claudet, had a specific gravity of 1.24, and held in a metre-cube, besides 144.0 kilograms of sulphate of soda, 64.0 of chloride of sodium, and 52.8 of copper as protochloride, besides small portions of zinc and iron, with a little lead, and 44 grams of silver. The above details of the salt-roasting process, which have often been published, are here repeated in order to bring more clearly before us the problem of separating the silver from the copper.

Various plans have been suggested for extracting from such solutions as the above the dissolved silver before throwing down the copper by metallic iron. It has been proposed to precipitate the silver by finely-divided metallic copper, as is done in the Augustin process from solutions of chloride of sodium holding only dissolved silver-chloride; but, since metallic copper at once converts protochloride into dichloride of copper, it becomes necessary, as a preliminary to the precipitation of the silver by this means, that the whole of the copper in the solution should first be brought into the latter condition. This may be effected by treating the hot solution with sulphurous acid, or by filtering it at a temperature near the boiling point through a layer of coarsely-ground copper matte, or of vitreous or purple copper ore, from which, as I have found, a second equivalent of copper is taken up. From solutions holding the whole of the copper as dichloride, the silver may be readily thrown down in the metallic state by filtering them through a layer of finely-divided

* Plattner, as is well known, showed that gold, like silver, is chloridized when pyritous ores containing it are roasted at a low red heat with common salt; an aurous chloride being apparently found, which, in the presence of chloride of sodium has a considerable degree of stability, though it is decomposed at higher temperatures. This chloride of gold is insoluble in water, and, unlike chloride of silver, is not decomposed by mercury. It is but slightly soluble in brine, though readily dissolved by a solution of hyposulphite of soda or lime. A process proposed by Kiss for the simultaneous extraction of silver and gold from pyritous ores is based on these reactions

metallic copper; but, inasmuch as the dichloride requires to hold it in solution, a great volume of hot concentrated brine,* this method of separating silver from solutions containing a considerable amount of copper is not in all cases practicable.

Among the plans which have been proposed for the separation of the silver from these saline solutions are those based on fractional precipitation. This is effected, as at Oker, by the use of sulphide of sodium; or better, by diluted sulphuretted hydrogen gas, as got by the action of air mixed with carbonic acid on the waste calcium-sulphide from Leblanc's soda-process. In the latter case, the whole of the silver is, according to Gibbs, carried down with the first six per cent. of the copper. Snelus blows finely-divided metallic iron into the solution, and finds the first twenty per cent. of copper thus precipitated holds four-fifths of the silver. For the extraction of the silver from the mixed sulphides it suffices to convert the silver into a sulphate, as in the Ziervogel process. For the separation of silver from precipitated copper, J. A. Phillips, by a process patented in 1877, makes the material into a paste with water and a mixture of common salt and carbonate of soda; and, after calcination in a reverberatory, gets the silver in the form of chloride, which is dissolved out by brine from the oxidized copper.

The solvent power of solutions of chloride of sodium for chloride of silver is diminished by dilution, and upon this fact, apparently, is based a process for the separation of silver, patented in 1877 in Great Britain by Jardine & Chadwick, which consists in diluting the strong lixivium from the salt-roasted ore to about specific gravity 1.10—1.12, and adding thereto, in the form of a dilute solution, about half a pound of acetate of lead to the ton of liquid. The precipitate, which after a time separates, consisting, in large part, of sulphate of lead, carries with it a portion of chloride of silver, and, it is said, a trace of gold.

The most elegant method for the separation of silver from these mixed solutions is, however, that patented by Claudet, and exten-

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* 100 cc. of a solution holding 15.0 grams of chloride of sodium, dissolve at 90° C., 10.0 grams; at 40°, 6.0; and at 14°, 3.5 grams of cuprous chloride; while 100 cc. of a solution holding 5.0 grams of chloride of sodium, dissolve at 90° 2.6 grams, and at 40°, 1.4 grams of cuprous chloride. This substance, contrary to the received statements, is not quite insoluble in water When the cuprous chloride is boiled with distilled water an amount equal to about 1.35 grams to a liter passes into solution, and is in part thrown down on cooling in a white crystalline form; the solution, at 14° C., still retaining about 0.90 grams to the liter. The above numbers are only approximations.

sively applied in Great Britain. It depends on the almost complete insolubility of iodide of silver in solutions of chloride of sodium, and consists in adding to the lixivium, in which the proportion of dissolved silver has previously been determined, a dilute solution of a soluble iodide just sufficient in amount to convert the whole of the silver into iodide of silver. The precipitate which separates after forty-eight hours of repose, is washed with dilute chlorhydric acid to remove adherent copper-salts, and then consists chiefly of a mixture of sulphate of lead with iodide of silver, which is reduced by metallic zinc, the iodine being thus recovered for further use. Treated in this manner, the calcined Spanish ores yield to the ton 20 grams of silver containing 1.3 per cent. of gold, amounting, according to Lunge, to about two-thirds the entire amount of precious metals contained in the ore. The presence of dichloride of copper in the solution interferes, by the production of a cuprous iodide, with the separation of the silver as iodide; and hence the calcination of the ores with salt must be so conducted as to give the copper in the condition of protochloride.*

The extraction of copper from its ores by roasting with salt is limited to pyritous ores poor in copper, which yield, by their previous calcination, a large proportion of peroxide of iron; the presence of this being necessary to the effectual chloridizing of the copper in the furnace. When applied to richer ores this method fails to render the whole of the copper soluble, for reasons which are made apparent by the investigations of Mr. Thomas Macfarlane, described by him in 1865. He found that while copper-ores, such as chalcopyrite and bornite, when calcined with salt, either alone or with an admixture of pulverized quartz, yield but a small portion of their copper in the form of soluble chloride, such a mixture of ore and salt, with twice its weight of peroxide of iron, and a little pyrites to furnish additional sulphur, if calcined at a low temperature, and without stirring, gave up nearly all its copper to water as a soluble chloride. It was made evident, from these and other experiments described by Macfarlane, that the mass of heated peroxide of iron, in the presence of air, favors the conversion of the sulphur into a sulphate, through which the decomposition of the common salt and the chloridizing of the copper is effected.†

* For an excellent account of wet processes for the extraction of copper, see Friedr. Bode, in Dingler's Polytechnisches Journal for January–March, 1877, vol. ccxxxi, pp. 254, 357, 428.

† Canadian Naturalist, second series, vol. ii, pp. 219–231, and vol. iii, p. 457.

These conditions are most fully realized when a material like the calcined residue of Spanish pyrites, containing in 100 parts about 4 parts each of copper and sulphur, and 80 parts or more of peroxide of iron, is calcined with a sufficient amount of common salt, in which case, as we have seen, the chloridizing of the copper is nearly complete. Ignorance of these conditions has more than once led to failure in attempts to apply this process of copper-extraction.

Unlike the method of chloridizing by roasting with salt, that depending on the use of a solution of ferrous chloride with salt is a general one, applicable to all naturally or artificially oxidized copper-ores, which may be readily and cheaply chloridized by its aid.* When applied to copper ores containing silver, however, this shares with the salt-roasting process the disadvantage that the silver is at the same time chloridized, and if not present in too large an amount, is dissolved, while the dichloride of copper formed by the reaction between the oxide of copper and the ferrous chloride precludes the use of Claudet's method of precipitating the dissolved silver by a soluble iodide.

There is a large class of copper-bearing ores and furnace-products containing, besides silver, and in some cases gold, portions of antimony and arsenic, often accompanied by lead, the treatment of which, either by the wet or the dry way, offers many difficulties. A simple and economical general method, which will effect a complete separation of copper from silver and gold on the one hand, and from arsenic, antimony, and lead on the other, has hitherto been a desideratum in metallurgy. From the want of such a process considerable quantities of refined copper extracted from western ores and mattes, and carrying from 40 to 50 ounces of silver per ton, have of late years been sold in our markets.

With my friend, Mr. James Douglas, Jr., of Phœnixville, Pa., I have devoted much time to the metallurgical problem thus presented, and as the result of our joint labors have now to bring before the Institute of Mining Engineers a novel wet process for the extraction of copper from its ores, which will, I think, be found to meet the required conditions. The new method is based upon the reaction described by Wöhler between sulphurous acid and a solution of protochloride of copper, which gives rise to insoluble dichloride with the elimination of one-half the chlorine in the form of

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* A process of copper-extraction, based on this principle, is the subject of United States letters-patent, granted to T. Sterry Hunt and James Douglas, Jr., February 9th, 1869.

chlorhydric acid, and the simultaneous formation of sulphuric acid, as simply expressed in the old notation by the formula

$$2CuCl + SO_2 + HO = Cu_2Cl + HCl + SO_3.$$

The resulting acid solution, when brought in contact with cupric oxide, will take up as much copper as it originally held, which may, in its turn, be thrown down by sulphurous acid. In this way, the solution of copper from an oxidized ore, and its precipitation as dichloride, may be repeated indefinitely, provided chlorine be supplied each time by the addition of a sufficient amount of some soluble chloride.

The reaction between sulphurous acid and a solution of protochloride of copper goes on slowly at ordinary temperatures, but is very rapid between 80° and 90° C. Solutions of sulphate of copper mixed with an equivalent of chloride of sodium, and holding 8.0 per cent. of copper, after being treated at 90° C. with an excess of sulphurous acid gas, retain less 1.0 per cent. of dissolved copper; while in the presence of an excess of sulphate of copper and sulphurous acid the precipitation of the chlorine from chloride of sodium is nearly complete; sulphate of soda and sulphuric acid remaining in solution in accordance with the equation

$$2CuO,SO_3 + NaCl + SO_2 = Cu_2Cl + Na,SO_3 + 2SO_3$$

The sulphurous-acid gas for effecting this reaction on a large scale is readily got in sufficient purity from the burning of iron-pyrites in the ordinary kilns used by the makers of sulphuric acid, care being that an excess of air be avoided. A Knowles pump, constructed for the purpose, has proved an efficient means of injecting the heated gas into the liquid. By this reaction we have found it easy, in repeated trials with a small experimental plant, to throw down in three hours' time 125 pounds of copper from an eight per cent. solution, the liquid still retaining about one per cent. of copper dissolved.

The acid liquors, when the reaction with sulphurous acid is complete, have exchanged their bright blue color for a pale green, and now contain in solution an excess of sulphurous acid, which must be got rid of before using them to dissolve a fresh portion of copper. This may be effected by keeping back a small portion of the chloridized copper-solution, and after the action of the gas is complete, as may be known by the changed color and the sulphurous odor of the liquid, adding the reserved portion thereto, by which means the excess of sulphurous acid will be oxidized. The chief part of the dichloride of copper separates during the passage of the gas, but a further portion is deposited on the cooling of the solution.

The excess of sulphurous acid may also be got rid of by blowing a current of hot air through the liquid after it has been withdrawn from the precipitated dichloride, and best while the process of saturating it with oxide of copper is going on. This, when got by the calcination of sulphuretted ores, contains more or less suboxide of copper,* which, with chlorhydric acid forms a portion of cuprous chloride, and the separation of this, under these circumstances, may be prevented by the action of atmospheric oxygen.

Cuprous chloride is quickly transformed into cupric oxychloride by atmospheric oxygen, and when dissolved or suspended in an acid liquid is by this means readily converted into a cupric salt, which may be again reduced to cuprous chloride by the action of sulphurous acid. In this way, like the nitric oxide in the leaden chamber, the cuprous chloride acts as a medium through which sulphurous acid and oxygen are made to combine and to form sulphuric acid. The two reactions of oxidation and reduction just described may go on alternately or simultaneously in the liquid, and thus it happens that when an excess of air enters the pyrites-kiln, so that considerable free oxygen passes with the sulphurous acid into the copper-solution, the dichloride is either separated slowly or not at all, while at the same time much sulphuric acid is formed. By taking advantage of these reactions between oxygen, sulphurous acid, and chloride of copper, we may at will increase the solvent power of our acid bath.

In applying this new process of copper-extraction to a roasted sulphuretted ore or matte, which we will suppose to contain a portion of silver, we begin by dissolving therefrom by water the sulphate, which, with proper care in roasting, should contain not less than one-third of the copper of the ore; taking care to add to the water enough of some soluble chloride to chloridize and render insoluble any sulphate of silver which may be present. From the clear lixivium thus obtained, after adding the requisite amount of chloride of sodium, the copper is precipitated, as already described, by the action of sulphurous-acid gas. The resulting acid liquid, freed from the excess of sulphurous acid by the addition of a reserved portion of the original solution containing copper-chloride, and still retaining more or less copper, is now used to dissolve the oxide of copper from a portion of the lixiviated ore; the process being

* I have found calcined sulphuretted copper-ores to contain, in addition to soluble cupric sulphate, and insoluble oxides of copper, a small portion of a cuprous compound, which, though insoluble in water, is dissolved by a hot and strong solution of common salt, and is probably a cuprous sulphate or sulphite.

aided by heat, and, if the formation of dichloride of copper is to be feared, by the injection of a current of air, which may be made the means of heating and agitating the mixture. If the ore contains silver, either in the form of metal or unoxidized sulphide, we have in the chloride of copper which is formed the best agent for bringing it to the condition of chloride of silver. This will be found in the residue after the extraction of the copper, together with any gold which may be present, lead as sulphate, oxides of antimony and iron, and earthy matters. Cobalt, nickel, and zinc, if present will, however, be dissolved, and not being precipitated by sulphurous acid, will, by successive operations, accumulate in the solution, and may afterwards be extracted.* From the residues thus deprived of copper we have found the silver to be readily dissolved by brine,† after which, if gold be present, it may be removed by chlorination, or the two precious metals may be extracted together from the residues by amalgamation. When, as in the case of certain mattes from Utah, for example, the residues contain a large amount of lead as sulphate, this may be recovered by smelting, and a base bullion got containing the precious metals. The same result may also be attained by smelting the residues with an admixture of a lead-ore.

Chloride of silver is soluble to some extent in solution of cupric chloride, and is then in part carried down with the cuprous chloride in the precipitation of the latter. The formation of cupric chloride may be avoided by adding to the solution of sulphate of copper little more than the amount of chloride of sodium necessary for the conversion of the copper into dichloride. In this case, as we have seen, the acid liquid after precipitation by sulphurous acid will contain chiefly sulphuric acid, though still holding sufficient cupric chloride to effect the chlordizing of any silver which may be present in the ore.

The dichloride of copper, as obtained by precipitation, is a white coarsely crystalline powder, having a specific gravity of 3.376 (Playfair and Joule), and, as we have seen (note on page 4), is nearly insoluble in cold water. After being washed from the acid liquid, it may be readily reduced by placing metallic iron in the moist dichloride, which should be covered with water to exclude the air. The action spreads rapidly through the precipitate, so that a single

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* For observations on the association of nickel and cobalt with certain copper-ores, see Appendix I.

† For notes on the solubility of chloride of silver in solutions of common salt and other chlorides, see Appendix II.

mass of iron will, in a few hours, change a considerable volume of dichloride around it into pure spongy metallic copper. The reduction of copper from solutions obtained in those wet processes where the copper exists as protochloride, often accompanied by salts of iron, entails a considerable loss of metallic iron, and gives a copper which is impure from the presence of basic iron-salts. The reduction of the solid dichloride, however, presents none of these disadvantages. Forty-five parts of iron suffice to reduce one hundred parts of copper; the precise ratio being as 28.0 : 63.4. The ferrous chloride which remains in solution may with advantage be used instead of chloride of sodium for chloridizing subsequent solutions of sulphate of copper, ferrous sulphate being formed which, as it accumulates, may be separated by crystallization from the acid liquid. The ferrous dichloride required to chloridize twenty parts of copper would equal about sixty-one parts of hydrated ferrous sulphate.

Another mode of treating the dichloride, which may in some cases be resorted to, consists in decomposing it, best at a boiling heat, with a slight excess of milk of lime. The dichloride is by this means converted into a dense orange-red suboxide of copper which, after being washed from chloride of calcium, in a filter-press or otherwise, and dried, may be readily reduced to metallic copper in a reverberatory furnace. For this reaction, 28.0 parts of pure quicklime are required for 63.4 parts of copper, and the resulting chloride of calcium may be used instead of chloride of sodium or chloride of iron for chloridizing solutions of sulphate of copper. In this case, there will be formed an insoluble sulphate of lime or gypsum, while the free sulphuric acid of the solution is replaced by chlorhydric acid. The use of the chloride of calcium would, however, require an additional operation, since, to avoid the presence of the precipitated gypsum either with the dichloride or the undissolved residue of the copper-ore, it would be necessary to add the chloride of calcium to the clear copper-solution, and, after allowing time for the gypsum to subside, to transfer the liquid to the vats in which the copper is to be precipitated by sulphurous acid. There may, however, be localities in which the cost both of metallic iron and of common salt is such as to render advantageous the decomposition of the dichloride of copper by lime, provided there is no silver to be extracted.

We have heretofore considered only the case in which the acid liquor got by precipitating the copper from neutral solutions in the form of dichloride is used to dissolve successive portions of oxide of copper alone. This can be done in the case of pure ores free from

other strongly basic oxides, if without loss, yet without any gain of acid save what comes incidentally from the portion of sulphuric anhydride which is given off in the calcination of pyrites, or from the reaction between sulphurous acid and oxygen in the presence of chloride of copper, as already explained. If, however, as is more often the case, we are treating artificially oxidized sulphuretted ores or mattes, which yield by roasting a mixture of oxide and sulphate of copper, it will be apparent that by the repeated use of the present process there must result a constantly augmenting proportion of free acid in the liquid.

This may be made clearer by examples. Let us suppose a solution holding in a cubic foot (equal 1000 ounces of water) 63.4 ounces or two equivalents of copper in the form of sulphate. To convert this into protochloride would require two equivalents or 117 ounces of chloride of sodium, but for the production of the dichloride, as we have seen, one equivalent, or a little more, will suffice, or, in place thereof, a corresponding amount of ferrous or calcic chloride. When, by the action of sulphurous acid, the whole of the copper is reduced to the cuprous condition, and in a great part thrown down as dichloride, the previously neutral solution will contain two equivalents or 98 ounces of sulphuric acid* (oil of vitriol), which, if a larger amount of chloride had been added, would be in part replaced by chlorhydric acid. These two equivalents of acid are capable of taking up two equivalents, or 79.4 ounces of oxide of copper, after which the solution will contain, as at first, 63.4 ounces of copper. If, however, we add to this acid solution, instead of simple oxide of copper, a calcined ore or matte in which one-third of the copper is present as soluble sulphate, and two-thirds as oxide, it is clear that when the acid is saturated we shall have in the liquid, besides the 63.4 ounces of copper from the oxide one-half as much more, or 31.7 ounces of copper which were already present as sulphate in the roasted ore; making in all three equivalents or 95.1 ounces of dissolved copper, which are, in their turn, to be converted into dichloride. Now, as the amount of acid set free in this reaction is equal to that originally combined with the copper, it follows that the liquid after the precipitation of the dichloride will contain three

* While we recognize the dyad nature of copper, oxygen and sulphur, and the bibasicity of sulphuric acid, it is simpler and more convenient for the calculations of the manufacturing chemist and the metallurgist to use, as we have done in the present paper, the older notation, and to speak of 31.7 parts of copper, 8 parts of oxygen, 40 parts of sulphuric oxide, 49 parts of oil of vitriol, 36.5 parts of chlorhydric acid, and 58.5 parts of chloride of sodium as equivalents.

equivalents of acid, instead of two as before. If to this we add, a second time, enough of the mixture of two-thirds oxide and one-third sulphate of copper to neutralize these three equivalents, we shall have four and a half equivalents of dissolved copper, from which, by a third repetition of the process of precipitation by sulphurous acid, four and a half equivalents of sulphuric acid would be set free; so that in place of 98 ounces we should have $220\frac{1}{2}$ ounces in the solution;—an amount which a fourth repetition of the process of saturation and precipitation would raise to six and three-quarter equivalents or 330 ounces of oil of vitrol.

If, instead of a mixture containing one-third of its copper as sulphate, we have one in which only one-fourth is sulphate and three-fourths are oxide, we should get by saturating with this a solution containing two equivalents of acid, and subsequent precipitation with sulphurous acid, a liquid holding 2.66 equivalents of free acid, which by a third repetition of the process would yield 3.55, and by a fourth 4.73 equivalents of free acid, in place of the 2.00 equivalents which were present after the first precipitation.

The above calculations are founded on the supposition that the roasted ore or matte contains, besides the oxide of copper, no base that would be attacked by dilute acids. In fact, however, oxides of lead, zinc and, more rarely, nickel and cobalt, may accompany the copper-oxide, and give rise, the first to an insoluble and the others to soluble sulphates, consuming more or less acid. Ores containing more or less carbonate of lime (often with carbonate of magnesia) are also of frequent occurrence, and here is seen a great advantage which this mode of copper-extraction possesses over all the other wet processes; for since lime and magnesia, and their carbonates, not only neutralize free acids, but throw down copper from its solutions, the treatment, by these processes, of ores containing any considerable proportion of calcareous matter is impracticable. With the process here proposed, which generates an abundance of free acid, the extraction of copper from ores which do not contain an excessive amount of calcareous matter presents no difficulty except such as arises from the mechanical obstacle created by the formation of gypsum in the solutions. The accumulation of acid in the bath is indeed so rapid in many cases that it will become unnecessarily strong, and may be diluted with water; while that portion not needed, after being deprived of the last portions of copper by the action of metallic iron, may be rejected unless it retains in solution other metals of value.

It will be seen from the foregoing description that the new process here described resembles those which, at the beginning of this paper, we have placed in Class II, inasmuch as the oxidized copper is separated from foreign metals by dissolving it in sulphuric and chlorhydric acids; with the difference, however, that the acids for this purpose are generated in the process itself, by the action of sulphurous acid, while the copper is separated from its solutions in the form of dichloride; the reduction of which to pure copper is readily effected by the consumption of a minimum amount of metallic iron. At the same time, any silver or gold which may be present in the ore is left undissolved, and in the best condition for subsequent extraction by well known methods, while the saving of cobalt and nickel, of lead, or of antimony, should these be present in quantities of economic importance, may be subsequently effected by very simple processes.

The apparatus for this new general method of copper-extraction is simple and inexpensive. The chlorine required in the precipitation of the copper being recovered for further use, the only reagent consumed, except the sulphurous acid—which is a waste product from the roasting of sulphurous ores—is an amount of iron which is equal to less than one-half the weight of the copper, and may be recovered in the form of sulphate of iron,—or, instead thereof, the same quantity of caustic lime.*

Appendix I.

The presence of small portions of cobalt and nickel in cupriferous pyrites is not uncommon, and mixed earthy oxides of copper, nickel, and cobalt have been found in considerable quantities in Missouri. A greenish, translucent, amorphous mineral, with black stains, resembling chrysocolla in appearance, from some place in western Nevada, where it was said to be abundant, and to have been mined for the manufacture of sulphate of copper, was brought to me in 1876, and found to contain considerable quantities of both cobalt and nickel. One of two closely agreeing analyses by my former pupil, Mr. Hardman, made at the Mass. Institute of Technology, in 1877, gave for this mineral as follows: Oxide of copper, 9.63; oxide of nickel, 3.23; oxide of cobalt, 3.88; peroxide of iron, 3.08; peroxide of manganese, 2.40; lime, 1.04; magnesia, 0.10;

* United States letters-patent, No. 227,902, for this method of copper-extraction were granted to Thomas Sterry Hunt and James Douglas, Jr., May 25th 1880.

alumina, 13.01; silica, 42.97; water, 18.38 = 97.72. The cobalt and nickel were separated by Rose's method. Another analysis, in which these metals were separated by the method of Fischer, with nitrite of potassium, gave of oxide of cobalt, 4.11. Such an ore, if abundant, would be a valuable source of both nickel and cobalt.

This aluminous mineral, like chrysocolla (*ante*, page 2) is attacked by a solution of ferrous chloride and common salt, by which the oxides of cobalt and nickel are indirectly dissolved; since, although they have not the power of decomposing ferrous chloride, they decompose the cupric chloride which is formed by its reaction with cupric oxide.

Appendix II.

As regards the solubility of chloride of silver in solutions of chloride of sodium, Vogel found that one liter of a saturated solution, at ordinary temperatures, held dissolved 0.950 grams of chloride of silver, while according to Hahn, a liter at 19.6° C. holds 1.269 grams. Becquerel found at ordinary temperatures for a similar solution 0.800 grams to the liter. 100 parts of water, saturated at 100° C., hold 26.61 parts, and at 15.6° C., 26.34 parts of chloride of sodium, the densities of the solutions being respectively 1206.93 and 1204.03. Hence, one liter of a saturated solution at 15.6° holds 316 grams of common salt, 1000 parts of which solution under these conditions dissolve, according to Hahn, at 15.6° C., 3.0 parts of chloride of silver; while, according to the observations of Vogel and of Becquerel, at "ordinary temperatures," not defined, 1000 parts, in saturated solution, dissolve respectively 4.0 parts and 2.53 parts of chloride of silver. The latter figure approximates to that given by Pelouze and Frémy, according to whom 1000 parts of salt at 18° C. hold dissolved 2.40 parts of chloride of silver. The solvent power, according to these chemists, varies greatly with the temperature, the amount dissolved being equal to 1.70 parts at 10° C., and not less than 6.80 at 100° C., while at 0° C. but traces of chloride of silver are dissolved. Differences of temperature may suffice to explain the discrepancies between the results of Vogel, Hahn, and Becquerel, but not those of Pelouze and Frémy at 18.0° C., a temperature above that mentioned by Hahn. It is possible that these chemists may not have employed solutions saturated with chloride of sodium, to which the observations of the others refer. Fresenius, speaking of the solubility of chloride of silver in hot concentrated solutions of the chlorides of sodium, potassium, am-

monium, calcium, zinc, etc., says "On sufficient dilution with cold water the dissolved portion separates so completely that the filtrate is not colored by sulphuretted hydrogen." *

As to the solubility of chloride of silver in some other chlorides, Hahn found that a liter holding 30.70 per cent. of ferrous chloride, and having a specific gravity of 1.419, dissolves, at 20° C., 2.385 grams of chloride of silver; while a solution, holding 44.48 per cent. of cupric chloride, and having a specific gravity of 1.5726, dissolves at 30° C., for 1 liter, 0.836 grams of chloride of silver. For farther observations on the solubility of chloride of silver in other chlorides, see Percy, *Metallurgy of Silver and Gold*, Part I, p. 58, and also Hahn, *Transactions American Institute Mining Engineers*, Vol. II, p. 99.

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* Fresenius, Quantitative Analysis, Amer. Ed., 1879, p. 124.